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(54) Title: METHOD FOR THE MANUFACTURE OF A COLOURED MARK

(57) Abstract

The invention relates to a method for the manufacture of an object with a coloured mark, by irradiating the surface of the object with laser light in the shape of the mark, with the object, in at least the area where the mark is applied, consisting of a plastic composition which contains at least three colour-forming components that lose their colour-forming capacity under the influence of laser light, which are chosen so and are present in such a concentration that at every wavelength between 400 and 700 nanometres at least a portion of the amount of incident light is absorbed, one or more colours being chosen for the mark, the wavelength of the laser light subsequently being set to a value that is dependent on the chosen colour and the surface of the object subsequently being irradiated with the laser light.

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# METHOD FOR THE MANUFACTURE OF A COLOURED MARK

The invention relates to a method for the manufacture of an object with a coloured mark, by irradiating the surface of an object with laser light in the shape of the mark.

Such a method is known from WO94/12352. That patent application describes a method according to which, under randomly chosen conditions, the surface of an object is irradiated with laser light so that a mark of an accidental colour is formed.

A problem involved in the known method is that the colours that are obtained are not freely chosen, but accidentally obtained. Furthermore, only a limited number of different colours is obtained.

The invention aims to provide a method that does not present the above drawbacks.

Surprisingly, this is achieved because at least the part of the object where the mark is applied consists of a plastic composition that contains at least three colour-forming components that lose their colour-forming capacity under the influence of laser light, which are chosen so and are each present in such a concentration that at every wavelength between 400 and 700 nanometres (nm) at least a portion of the amount of incident light is absorbed, one or more colours being chosen for the mark, the wavelength of the laser light subsequently being set to a value that is dependent on the chosen colour and the surface of the object subsequently being irradiated with the laser light.

With the aid of the method according to the invention marks of any or almost any predetermined colour can be obtained, simply by setting the wavelength of the laser light to a value determined for that purpose.

It is for example possible to irradiate the surface of the object with laser light having a series of different wavelengths before carrying out the method according to the invention, so as to determine a relationship between the wavelength of the laser light and the colour of the mark obtained. Then the wavelength of the laser light can be set to a value dependent on the chosen colour on the basis of the relationship thus obtained.

'Colour-forming components' are understood to be components that have a chromatic colour, such as colourants and pigments. White or black components, including for example titanium dioxide, chalk, barium sulphide, carbon black or iron sulphide, are not understood to be included in the range of colour-forming components.

The plastic composition may in general contain any thermoplastic or thermosetting plastic or any elastomer. Very suitable are the plastics which the plastic composition in WO94/12352 may contain.

Preferably, the colour-forming components are each present in such a concentration that at every wavelength between 400 and 700 nm at least 20%, more preferably at least 50% and even more preferably at least 80%, of the amount of incident light, expressed in lux, is absorbed.

A person skilled in the art will be able to easily choose the colour-forming components and the concentration, measure the amount of light absorbed at every wavelength between 400 and 700 nm (the absorption spectrum) with the aid of one of the known measuring methods and then adjust the colour-forming component

and its concentration until the desired absorption spectrum is obtained.

The method according to the invention can be carried out with the aid of one or more laser apparatuses, which irradiate laser light with a wavelength that corresponds to the value chosen for the wavelength on the basis of the desired colour of the mark.

Preferably, the method according to the invention is carried out with the aid of a laser apparatus with an adjustable wavelength. With such an apparatus the wavelength required for the colour chosen for the mark can easily be set. It is then also possible to obtain a mark containing more than one colour with the aid of one apparatus.

Preferably, the surface of the plastic composition is irradiated with laser light at at least three different wavelengths, more preferably at a multitude of wavelengths, which are dependent on the colours chosen for the mark. As a result, marks are obtained that contain a multitude of colours and may even approach or, if use is made of a laser beam with a very small cross-section, even surpass the quality of a colour photograph. Very good results are obtained if the cross section of the laser beam is equal to or smaller than the grain diameter of a colour photograph. A characteristic value for such a grain diameter is 0.5-3 micrometres.

Preferably, the plastic composition according to the invention contains only colour-forming components that lose their colour-forming capacity under the influence of laser light and the colour-forming components have each one single absorption band (the concept 'absorption band' is described in Colour Chemistry, 2nd edition, H. Zollinger, VCH Verlag Weinheim, Germany (1991), ISBN 3-527-28352-8).

That ensures that the wavelength of the

colour in which the mark is obtained corresponds to the wavelength of the laser light with which the surface of the plastic composition is irradiated. In that way it is very easy to obtain the chosen colour, because the chosen colour will practically correspond to the colour of the laser light.

The colour chosen for the mark will correspond more or even entirely to the colour of the laser light if the colour forming components and their concentrations are choosen so that, between 400 and 700 nm, at least approximately the same amount of light is absorbed at every wavelength. Preferably the amounts of light absorbed per wavelength differ not more than 20% from one another, more preferably 10%, even more preferably 5%. The surface of the object additionally has a neutral grey or black colour before the mark is applied.

Very good results are obtained when the plastic composition contains a first colour-forming component that reflects light whose main colour is yellow, a second colour-forming component that reflects light whose main colour is magenta and a third colour-forming component that reflects light whose main colour is cyan.

Preferably, the colour-forming components have a comparable bleaching efficiency for the laser light. 'Bleaching efficiency' is understood to be the length of time it takes a colour-forming component, irradiated with laser light of a certain intensity, to lose 80% of its light-absorbing capacity, light absorbing capacity being the quotient of (1 - amount of reflected light) and the amount of incident light, both expressed in lux. Preferably, the different components' bleaching efficiencies do not differ more than 20% from one another, more preferably not more than 10%. That ensures that during the method, if a mark having more than one colour is applied, only the wavelength of the

laser apparatus or laser apparatuses will have to be set per colour and for example the duration of the treatment and the intensity of the laser light may simply have the same value for every colour.

It is also important that the colour-forming components do not or virtually not lose their colour-forming capacity under normal daylight. Therefore the colour-forming components preferably have a colour stability of at least 3, more preferably at least 5, on Wool's scale (according to DIN 54003).

The invention also relates to an information carrier, at least one surface of which consists of the plastic composition described above and preferably at least 50% of which surface is covered with one or more marks.

Such an information carrier can be provided with a mark with the aid of the method according to the invention. The mark may contain any desired colour. The mark may even have the form of a true-to-nature representation of for example objects, animals or persons. It is also possible for at least 50% of the surface of the information carrier to be covered with text.

Examples of such information carriers are posters, signboards, company signs, advertisement boards, etcetera.

Preferably, the information carrier has a supporting layer, which supports the layer consisting of the plastic composition. That way the layer consisting of the plastic composition may have a small thickness and different types of information carriers, depending on the type of supporting layer chosen, are obtained for all kinds of purposes. The supporting layer may for example consist of paper and the information carrier may have the form of a colour photograph or a photocopy. The supporting layer may also consist of a plastic or a metal. Preferably the plastic of the

plastic composition is chosen so that it adheres well to the supporting layer.

The invention also relates to an object that is to be processed into the information carrier described above.

Example I

A dry blend was prepared from 1897 parts by weight of Ronfalin$^{R}$ SFA-34, an acrylonitrile-butadiene-styrene copolymer (ABS) supplied by DSM, the Netherlands, 100 parts by weight of Tiofine$^{R}$ R41, a titanium dioxide pigment supplied by Tiofine, the Netherlands, and 1 part by weight of Irgalith$^{R}$ Rubine 4 BP, 1 part by weight of Irgalith Blue LGLD and 1 part by weight of Cromophtal$^{R}$ Yellow 6G, magenta, cyan and yellow pigments, respectively, supplied by Ciba-Geigy, the Netherlands.

With the aid of a ZSK$^{R}$ 30 twin-screw kneader, supplied by Werner and Pfleiderer, Germany, the dry blend was melted, kneaded at 260°C and processed into granulate. The granulate was injection-moulded into plates measuring 3.2*120*120 mm with the aid of an Arburg Allrounder$^{R}$ 320-90-750 type of injection-moulding machine, at a temperature of 240°C.

The coloured pigments in the plates absorb the visible light. The plates had a light grey colour.

Subsequently marks were applied to the surface of the plates with the aid of a laser setup. Use was made of a tunable multi-wavelength laser setup (TMW laser setup). The laser setup contained an EEO$^{R}$-355 type of seeding laser, which was used as a pump laser for a GCR$^{R}$-230/50 type of Nd:YAG laser. The laser setup also included a MOPO$^{R}$ 710 type of optical parameter oscillator (OPO), which received the signal from the latter laser via a frequency doubling optic (FDO). The setup was supplied by Spectra-Physics, USA. The following laser settings were chosen:

Pulse length: 10 ns
Q switch frequency: 10 Hz
dot diameter: 8 mm
Writing speed: 30 mm/s
line distance: 5 mm.
Square marks measuring 20*20 mm were applied to the surface of the sample plates with the aid of the laser setup. The wavelength λ of the laser light irradiated by the laser setup was set for the colour previously chosen for the mark. The spectra of the light reflected by the marks were determined with the aid of a DATA COLOUR$^{R}$ Micro-Flash 200-D reflection meter, supplied by DAT COLOUR. The spectra were found to have the shape of a single peak. The wavelength of the maximum of the peak ($\lambda_{max}$) was determined. The wavelength of the maximum corresponds to the colour perceived by the eye. The results are shown in Table 1. The surface of the plates was not affected by the application of the marks in the area of the marks.

Example II

Example I was repeated, only Stamylan P$^{R}$ 83 MF 10, a polypropylene supplied by DSM, the Netherlands, was used instead of ABS.
The results are shown in Table 1.

Example III

A dry blend was prepared from 98.74 parts by weight of Arnitel$^{R}$ TV4 261, a polybutylene terephthalate supplied by DSM, the Netherlands, 0.03 parts by weight of Paliogen$^{R}$ Red K 3911 HD, a red pigment supplied by BASF, the Netherlands, 0.75 parts by weight of Meteor Plus$^{R}$ Teal Blue, a cyan pigment supplied by Engelhard, Germany, 0.03 parts by weight of PV Echtgelb$^{R}$ HG, a yellow pigment supplied by Hoechst, the Netherlands, 0.3 parts by weight of Kronos$^{R}$ CL 220, a titanium dioxide pigment supplied by Kronos, the

Netherlands, and 0.15 parts by weight of magnesium stearate.

The dry blend was injection moulded into plates as described in Example I, only at a temperature of 260°C. The plates had a moss grey colour. The surface of the plates was provided with marks as described in Example I. The results are shown in Table 1.

Example IV

A lacquer was prepared in a beaker by vigorously stirring 65.0 parts by weight of Uracron$^{R}$ HDT EV 412, a hydroxyl-functional resin supplied by DSM Resins, the Netherlands, 20.8 parts by weight of Tolonate$^{R}$ HDT EV 412, supplied by Hüls, Germany, 0.6 parts by weight of dibutyl tin laureate, supplied by Aldrich, Belgium, 10.0 parts by weight of Kronos$^{R}$ CL 220, 1.2 parts by weight of Cromophtal$^{R}$ Yellow 3G, a yellow pigment supplied by Ciba-Geigy, the Netherlands, 1.2 parts by weight of Paliogen$^{R}$ Red L 3910 HD, a red pigment supplied by BASF, the Netherlands, and 1.2 parts by weight of Orasol$^{R}$ Blue GN, a blue pigment supplied by Ciba-Geigy, the Netherlands. The lacquer was applied to an aluminium plate in a layer with a thickness of 50 micrometres. The lacquer layer had a grey colour. Marks were applied in the lacquer layer as described in Example I, only the line distance was set to 1 mm. The results are shown in Table 1.

Example V

Example IV was repeated, only the concentrations of the yellow and the blue pigment were raised to 1.8 parts by weight. The lacquer layer had a green colour. The results are included in Table 1.

TABLE 1

| Laser settings | Example I | Example II | Example III | Example IV | Example V |
|---|---|---|---|---|---|
| λ (nm)/ colour | $\lambda_{max}$ (nm) from reflection spectra | | | | |
| 430/ violet | 428 | 425 | 436 | 427 | 430 |
| 470/ blue | 475 | 471 | 481 | 468 | 490 |
| 575/ yellow | 580 | 575 | 585 | 572 | 520 |
| 650/ orange | 645 | 655 | 662 | 643 | 680 |

The results in Table 1 show that the colours of the marks are determined by the wavelength of the laser light. In the case of the grey plates the position of the maximum of the marks' reflection spectrum (and hence the colour perceived by the eye) even corresponds to the wavelength of the laser light.

## CLAIMS

1. Method for the manufacture of an object with a coloured mark, by irradiating the surface of the object with laser light in the shape of the mark, with the object, in at least the area where the mark is applied, consisting of a plastic composition which contains at least three colour-forming components that lose their colour-forming capacity under the influence of laser light, which are chosen so and are present in such a concentration that at every wavelength between 400 and 700 nanometres at least a portion of the amount of incident light is absorbed, one or more colours being chosen for the mark, the wavelength of the laser light subsequently being set to a value that is dependent on the chosen colour and the surface of the object subsequently being irradiated with the laser light.
2. Method according to Claim 1, characterized in that the method is carried out with the aid of a laser apparatus with an adjustable wavelength.
3. Method according to Claim 1 or Claim 2, characterized in that the surface of the object is irradiated with laser light at at least three different wavelengths.
4. Method according to any one of Claims 1-3, characterized in that the plastic composition contains only colour-forming components which lose their colour-forming capacity under the influence of laser light and that the colour-forming components have one single absorption band.
5. Method according to any one of Claims 1-4, characterized in that the colour forming component and their concentrations are chosen so that the amounts of light that are absorbed per wavelength between 400 and 700 nanometres differ from one

another by not more than 20%.

6. Method according to any one of Claims 1-4, characterized in that the amounts of light that are absorbed per wavelength between 400 and 700 nanometres differ from one another by not more than 5%.

7. Method according to any one of Claims 1-6, characterized in that the plastic composition contains a first colour-forming component that reflects light whose main colour is yellow, a second colour-forming component that reflects light whose main colour is magenta and a third colour-forming component that reflects light whose main colour is cyan.

8. Method according to any one of Claims 1-7, characterized in that the bleaching efficiencies of the colour-sensitive components differ from one another by not more than 20%.

9. Information carrier, at least one surface of which consists of the plastic composition as described in Claims 1-8, at least 50% of that surface being covered with one or more marks.

10. Object that is to be processed into the information carrier according to Claim 9.

# INTERNATIONAL SEARCH REPORT

Int. ional Application No
PCT/NL 96/00197

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M5/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41M G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | WO,A,94 12352 (DSM N.V.) 9 June 1994<br>cited in the application<br>see examples 1,2,5-7<br>see claims 1-19<br>see page 4, line 8 - page 7, line 8<br>--- | 1-10 |
| X | EP,A,0 413 664 (CIBA-GEIGY AG) 20 February 1991<br>see page 3, line 38 - page 4, line 26;<br>claims 1-12; example 1<br>--- | 1-10 |
| X | EP,A,0 327 508 (CIBA-GEIGY AG) 9 August 1989<br>see page 2, line 36 - page 4, line 22;<br>claims 1,14; example 1<br>---<br>-/-- | 1-10 |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP,A,0 190 997 (CIBA-GEIGY AG) 13 August 1986<br>see page 2, line 6 - line 13<br>see page 3, line 25 - page 4, line 22;<br>claim 1<br>----- | 1-10 |

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Information on patent family members

Int. onal Application No
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| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
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